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ELECTROCHEMICAL BEHAVIOUR OF CADMIUM
IN THE H_2O - D_2O SYSTEM
I. POLAROGRAPHIC STUDY

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J. Alonso-López

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I. POLAROGRAPHIC STUDY

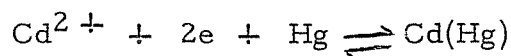
ALONSO-LOPEZ, J.[✉]

INTRODUCTION

In the course of certain "Critical Experiments" being carried out on a nuclear reactor programme using D₂O of 99.7 per cent purity, anomalous results were observed, which were thought to arise from contamination of the D₂O due to corrosion of a neutron-detector cadmium foil

Preliminary polarographic determinations of Cd²⁺ in a sample of this D₂O showed that, for any given concentration of Cd²⁺, the values of the limiting current were considerably smaller than expected.

The present study aims at establishing to what extent the electrode process



is affected by the presence of D₂O. The variation of the limiting current with D₂O concentration is also investigated.

EXPERIMENTAL TECHNIQUE AND PROCEDURE

Apparatus and reagents

All polarograms were recorded on a Sargent Polarograph, Mod. XXI (E. H. Sargent and Co., Chicago), equipped with a conventional electrolytic cell for work at controlled temperature.

The characteristics of the capillary tube (measured in 0.1 M KCl and

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with the mercury reservoir at a height of 60 cm) were $m = 3.01 \text{ mg/s}$ and $t = 3.1 \text{ s}$.

A saturated calomel electrode and/or a mercury-pool electrode were used as reference electrodes.

Dissolved air was removed from the solution by passing a current of pure dry N_2 for 30 min.

Experiments were carried out at temperatures of 25, 35 and 50 °C (± 0.1 °C) using a Höppler Thermostat, Mod. NB.

All reagents were of the highest purity: Merck, A.R., twice-distilled mercury, and 99.7 per cent D_2O (supplied by the Engineering Division of J.E.N.).

Experimental procedure

Samples for polarographic determinations were prepared in the usual manner. Solutions were 0.1 M $\text{KCl} + 0.01 \text{ M HCl}$, and $3.5 \times 10^{-4} \text{ M Cd}^{2+}$. No maximum suppressor was required. In the $\text{H}_2\text{O}-\text{D}_2\text{O}$ media, the D_2O concentration was varied from 96 per cent to 20 per cent by weight.

Additions of D_2O to the different solutions were made inside a glove-box, to prevent any alteration in the concentration of the stock solution of heavy water (99.7 per cent). The D_2O concentration of the solutions was checked after each experiment by infra-red analysis.

Quintuplicate polarographic determinations were made with all samples. The results were compared with those from comparable solutions containing no D_2O obtained under identical conditions. The sensitivity of the instrument was kept constant (whenever possible) throughout the experiments.

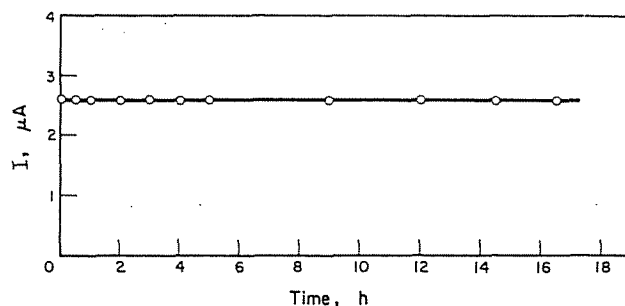


FIG. 1. Limiting current as a function of time.
 $3.5 \times 10^{-4} \text{ M Cd}^{2+}$ and 50.11 per cent (by weight) D_2O with 0.1 M $\text{KCl} + 0.01 \text{ M HCl}$ as supporting electrolyte; $25 \pm 0.1^\circ\text{C}$.

RESULTS

Limiting current as a function of time

The time dependence of the limiting current was studied on a sample containing 50.11 per cent by weight of D_2O . Figure 1 shows the values after different time intervals, up to 17 h. The constancy with time is evident, showing that the process remains unaltered throughout the experiment.

Variation of limiting current with drop time

The value of the limiting current was measured at different drop times, in a solution containing 96.07 per cent D_2O , and compared with corresponding values in a solution with ordinary water. These experiments were conducted at a number of temperatures.

The drop time was varied from 1 to 7 s per drop, the value being adjusted at a constant potential of -0.65 V(sce). The results are shown in Fig. 2. The continuous curves are for solutions in 96.07 per cent D_2O and the discontinuous curves are for solutions in ordinary water, at the different temperatures. The curves for D_2O and for H_2O are of similar shape, but those for D_2O always lie below the corresponding ones for H_2O .

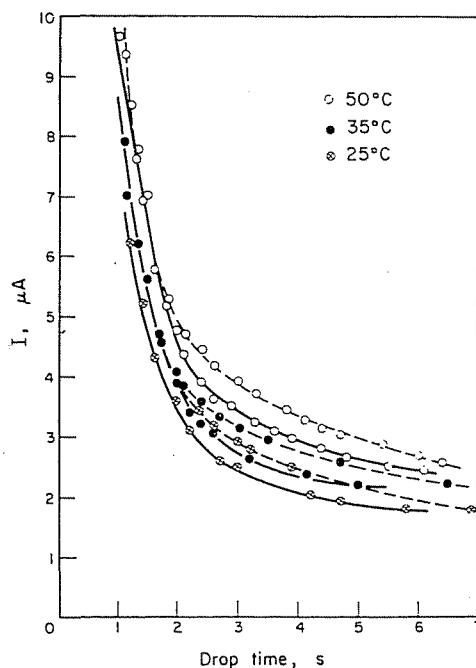


FIG. 2. Variation of limiting current with drop time.
 3.5×10^{-4} M Cd^{2+} with 0.1 M KCl + 0.01 M HCl as supporting electrolyte.
 —, 96.07 per cent D_2O . ---, normal water.

Variation of limiting current with temperature

Figure 3 shows a plot of I vs T for a drop time of 3.1 s per drop. This plot yields two non-parallel straight lines, from which the temperature coefficients of 1.3-1.5 per cent for a 1° rise in temperature for D_2O , and 1.1-1.3 per cent for H_2O , have been obtained.

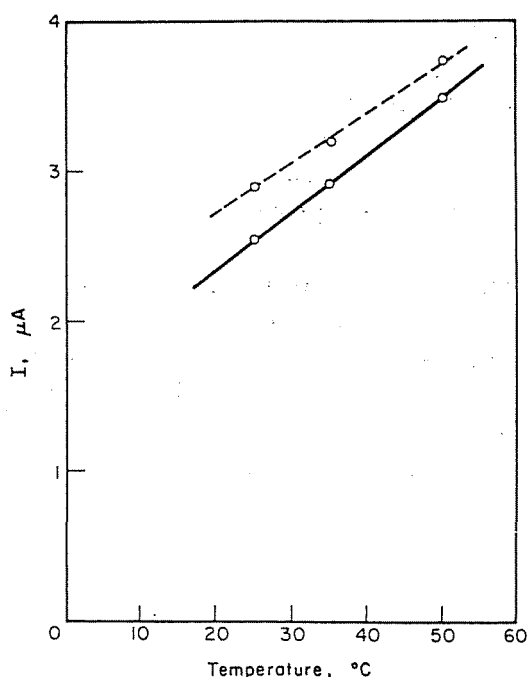


FIG. 3. Variation of limiting current with temperature.
 3.5×10^{-4} M Cd^{2+} with 0.1 M KCl + 0.01 M HCl as supporting electrolyte.
 —, 96.07 per cent D_2O
 ---, 100.00 per cent H_2O

Reversibility and half-wave potential

Figure 4 shows a plot of I vs E obtained from a solution in 95.00 per cent D_2O (curve B) and from a similar solution in H_2O (curve A). Despite a significant difference in the values of i_d , both curves have the same shape, which is the characteristic shape of a reversible electrode process.

The half-wave potentials of both solutions were -0.61 V(sce).

Variation of limiting current with D_2O concentration

The decrease in the value of the limiting current produced by changing the solvent (Figs. 2 and 4), was studied as a function of the D_2O concentration.

The results presented in Fig. 5 are for 25 °C. I_H is the limiting current

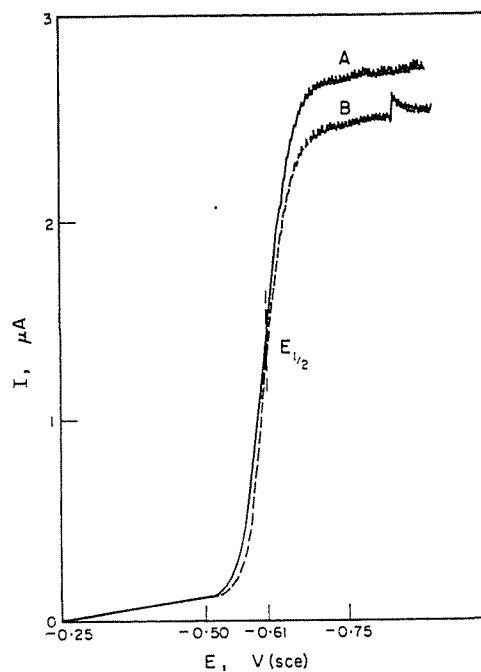


FIG. 4. Reversibility and half-wave potential.
 $3.5 \times 10^{-4} \text{ M Cd}^{2+}$ with $0.1 \text{ M KCl} + 0.01 \text{ M HCl}$ as supporting electrolyte;
 $25 \pm 0.01^\circ\text{C}$.
 A, normal water.
 B, 95.00 per cent D_2O .

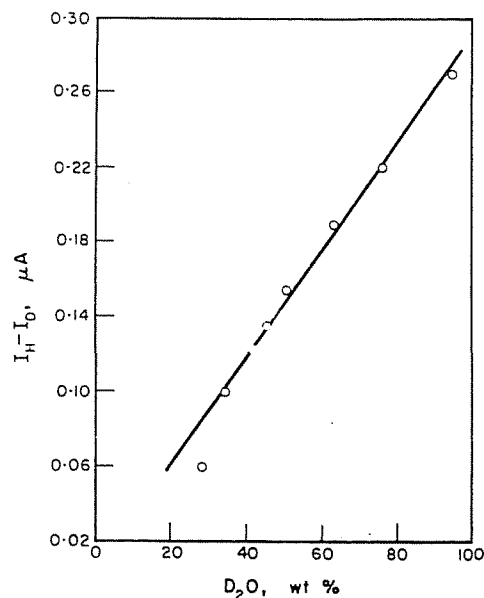


FIG. 5. Dependence of diffusion current on D_2O concentration.
 $3.5 \times 10^{-4} \text{ M Cd}^{2+}$ with $0.1 \text{ M KCl} + 0.01 \text{ M HCl}$ as supporting electrolyte;
 $25 \pm 0.0^\circ\text{C}$.

observed when the solvent is water and I_D is the value observed when the solvent contains the amount of D_2O given by the abscissa. The plot is linear at D_2O concentrations higher than 35 per cent. For concentrations lower than 35 per cent, instrumental errors were of the same magnitude as the expected values of $I_H - I_D$.

Similar experiments were conducted at temperatures of 35 °C and 50 °C. The results obtained were reproducible, but the values of $I_H - I_D$ were non-linear with respect to the D_2O concentration.

DISCUSSION

Although the electrode behaviour of the supporting electrolyte used is sufficiently well established in ordinary aqueous solutions¹⁻⁶, there is no data in the literature about possible deviations in the presence of D_2O . For this reason, the 0.1 M KCl + 0.01 M HCl concentration was kept constant in all the solutions studied. From the results presented in Figs. 1, 2, 3 and 4, the hypothesis that the decrease in limiting current may be due to absorption on the electrode must be discounted. The electrode process has the characteristics of a diffusion-controlled process, so that the measured current must be due only to diffusion of cadmium ions.

The curves in Fig. 2 differ from those obtained by Meites and Meites,⁶ who found that the diffusion current increased with drop time when this was greater than 4.5s. The absence of this effect may be due to the different concentration of HCl used.

In a study of the polarographic characteristics of Cd^{2+} in ordinary aqueous solutions, Lingane⁴ found that the value of the diffusion current depended on the HCl concentration in the supporting electrolyte. He attributed this to the formation of several cadmium chloride complexes.

In $H_2O - D_2O$ mixtures, D_2O molecules may be expected to replace some of the H_2O molecules in the solvation sheaths of the complexes, and the corresponding increase in molecular weight could contribute to the observed differences in the diffusion current.

Studying the influence of viscosity on diffusion current for Cd^{2+} and several other metal ions in aqueous solutions of H_2SO_4 , NaOH and Na_2SO_4 , Brasher and Jones⁷ found that the diffusion current was inversely proportional to the square root of the viscosity of the medium. Therefore, viscosity changes due to the presence of D_2O in the system may also influence the value of the diffusion current.

It may be concluded that both substitution of H_2O by D_2O in the solvation sheaths of the complexes and changes in the viscosity of the medium affect the diffusion coefficient of the cadmium ions to give the observed decrease in the

values of the diffusion current, and further research is now being conducted to determine the relative importance of these two factors.

Figure 5 shows that, for the conditions studied, the decrease in diffusion current is proportional to D_2O concentration. This relation may be used as a means of determining the concentration of D_2O in $D_2O - H_2O$ mixtures. With an instrument of higher sensitivity than the one used here, more accurate results should be obtained and the D_2O concentration range could be extended.

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"Comportamiento electroquímico del cadmio en el sistema H_2O-D_2O . - I. Estudio polarográfico".

ALONSO-LOPEZ, J. (1966) 7 pp 5 figs. 7 refs.

Se ha estudiado la corriente de difusión del Cd^{2+} en el sistema H_2O-D_2O y en un medio electrolito soporte de ClK 0,1 M $\downarrow$ ClH 0,01 M; en función de los parámetros tales como : tiempo, altura del depósito de mercurio y temperatura de dicho electrolito. Las características encontradas, responden a un proceso reversible de difusión controlada.

En el sistema H_2O-D_2O , los valores de la corriente de difusión resultaron mas pequeños que los correspondientes al H_2O a 25 °C. Esta disminución es proporcional a la concentración de D_2O para concentraciones de esta superiores al 35%. Este hecho, puede tener aplicación analítica en la determinación de D_2O en dichas mezclas.

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